EFFECT OF CAPILLARY DIMENSIONS ON DIE SWELL OF MOLTEN POLYMERS

EFFECT OF CAPILLARY DIMENSIONS ON DIE SWELL OF MOLTEN POLYMERS

27 55 72

By

Dang, Huu Thanh, B. Sc.

Sumarke

A Project Submitted to the Faculty of Graduate Studies In Partial Fulfilment of the Requirements For the Degree Master of Engineering

McMaster University

January, 1974

MASTER OF ENGINEERING (1974) (Chemical Engineering) McMaster University Hamilton, Ontario

TITLE: EFFECT OF DIE DIMENSIONS ON DIE SWELL OF MOLTEN POLYMERS

AUTHOR: Dang Huu Thanh, B. Sc.

SUPERVISOR: Dr. J. Vlachopoulos

NUMBER OF PAGES: 95

.

ABSTRACT

The effect of capillary dimensions on the die swell of molten polymers is investigated. Low and high density polyethylene, polypropylene, polystyrene are used to make investigation It is found the die swell decreases with L/D. The plot of die swell index (d/D) vs. L/D has the shape of an exponential decay curve.

Bagley's decaying equation is used to fit the data. The effect of Deborah number on die swell phenomenon is also studied. The relationship between the recoverable shear strains of infinitely long capillary and the one with dimensions ratio L/D is obtained. This relationship could be used to estimate the die swell of short capillary from its value at equilibrium and polymer characteristics.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to his research advisor, Dr. John Vlachopoulos for his constant guidance and advice in data interpretation, and most of all, for his encouragement.

Gratitude is also due to the Department of Chemical Engineering, McMaster University, for its financial support to the author.

TABLE OF CONTENTS

		PAGE
I	Introduction	1
II	Literature Survey 2.1) Experimental Observations 2.2) Some proposed mechanisms for die swell	4 6
III	<pre>Theoretical Background 3.1) Expressions predicting die swell 3.2) Capillary flow 3.3) Errors in Capillary flow 3.3.1) End effects 3.3.2) Slip at the wall 3.3.3) Heat effects</pre>	9 12 16
IV	<pre>Experimental Procedure 4.1) Equipment 4.2) System operation 4.3) Materials 4.4) Treatment of Data 4.4.1) Shear diagram 4.4.2) Melt fracture 4.4.3) Extrudate swelling (</pre>	19 19 21 23 23 23 28
V	Results 5.1) Reproducibility 5.2) Effect of temperature on die swell 5.3) Effect of shear stress and shear rate on die swell 5.4) Effect of molecular weight distributions on die swell 5.5) Effect of capillary dimensions on die swell	33 34 36 36 43
VI	<pre>Analysis and Discussion 6.1) Bagley's suggestion 6.2) Effect of Deborah number on die swell 6.2.1) Time constant 6.2.2) Definition of Deborah number 6.2.3) Effect of Deborah number on polymer processing 6.3) Relationship between average recoverable shear strain of a short and long capillary</pre>	49 57 60 60 61
VII	Conclusions	7 8
VIII	Suggestions	79
IX	Nomenclature	80
х	References	83
XI	Appendices	86
	Experimental Data	86

LIST OF FIGURES

Figure	1.1	Schematic illustration of die swell phenomenon.	PAGE 3
Figure	1.2	Decay of die swell with capillary dimensions	3
Figure	3.1	Schematic illustration of the flow in a capillary tube	13
Figure	3.2	Correction of tube length, L, by the addition of length ND	17
Figure	4.1	Plot of pressure vs. L/D of capillary	24
Figure	4.2	Plot of true shear stress versus pseudo shear rate	25
Figure	4.3	Plot of true shear rate versus true shear stress (LDPE)	26
Figure	4.4	Plot of true shear rate versus true shear stress (HDPE)	27
Figure	4.5	<pre>Plot of pseudo shear rate versus true shear stress on logarithmic scale .1) Low density polyethylene .2) High density polyethylene .3) Polypropylene .4) Polystyrene</pre>	30 30 31 31
Figure	4.6	Velocity profiles for the isothermal flow of power law fluids through tubes	32
Figure	5.1	Effect of temperature on die swell	35
Figure	5.2	Effect of shear stress on die swell .1) Low density polyethylene .2) High density polyethylene .3) Polypropylene .4) Polystyrene	37 38 39 40
Figure	5.3	Effect of molecular weight distribution on die swell	42
Figure	5.4	Effect of L/D on die swell of LDPE	44
Figure	5,5	Effect of L/D on die swell of HDPE	45
Figure	5.6	Effect of L/D on die swell of Polypropylene	46
Figure	5.7	Effect of L/D on die swell of Polystyrene	47
Figure	5.8	Effect of L/D on die swell of standard Polystyrene	48

Figure	6.1	Bagley's exponential decay equation is used to fit data for LDPE	52
Figure	6.2	Bagley's exponential decay equation is used to fit data for HDPE	53
Figure	6.3	Bagley's exponential decay equation is used to fit data for Polypropylene.	54
Figure	6.4	Bagley's exponential decay equation is used to fit data for Polystyrene.	55
Figure	6.5	Definition of time constant of a polymeric system.	59
Figure	6.6	Plot of die swell index vs. average residence time, LDPE	62
Figure	6.7	Plot of die swell index vs. average residence time. HDPE	63
Figure	6.8	Plot of die swell index versus average residence time. Polypropylene	64
Figure	6.9	Plot of die swell index versus average residence time. Polystyrene	65
Figure	6.10	Plot of average recoverable shear strain vs. pseudo shear rate. LDPE	67
Figure	6.11	Plot of average recoverable shear strain vs. pseudo shear rate. HDPE	68
Figure	6.12	Plot of average recoverable shear strain vs. pseudo shear rate. Polypropylene	69
Figure	6.13	Plot of average recoverable shear strain vs. Pseudo shear rate. Polystyrene	70
Figure	6.14	Plot of Ln ($\frac{\overline{\sigma_{L/P}}}{\overline{\sigma_{\infty}}}$) vs. L/D for LDPE	73
Figure	6.15	Plot of Ln $(\frac{\overline{\sigma_{L/D}}}{\overline{\sigma_{\infty}}})$ vs. L/D for HDPE	74
			;

LIST OF TABLES

									PAGE	
Table 4	• 1	Table o	f Capillarie	s us	sed				20	
Table 4	•2	Table o	f Materials	used	1				22	
Table 6	5.1	Table o	f parameters	of	Equation	(6.5)	for 1	LDPE (0701)50	
Table 6	5.2	Table o	f parameters	of	Equation	(6.5)	for]	LDPE (0118)) 50	
Table 6	5.3	Table o	f parameters	of	Equation	(6.5)	for I	HDPE(7930)	51	
Table 6	5.4	Table o Polypro	f parameters pylene	of	Equation	(6.5)	for		51	
Table 6	5.5	Table o Polysty	f parameters rene(HF-55)	of	Equation	(6.5)	for	ž.	51	
Table (5.6	Table o Polysty	f parameters rene (HT42.1	of)	Equation	(6 . 5)°	for		56	
Table 6	5.7	Table o plot o	f exponent o vs. G.	f po	ower law 1	fluid a	nd sl	lope of	71	
Table 6	5.8	Table o	f parameters	of	Equation	(6.11)	for	LDPE	72	
Table 6	5.9	Table o	f parameters	of	Equation	(6.11)	for	HDPE	75	
Table 6	5.10	Table o	f parameters	of	Equation	(6.11)	for	Polypropy	lene	75
Table 6	5.11	Table o	f parameters	of	Equation	(6.11)	for	Polystyre	ne	75

I INTRODUCTION

It is generally observed that when a molten polymer is forced from a reservoir, through a capillary, the extrudate diameter is not equal to the capillary diameter. (Figure 1.1). This phenomenon is known as "die swell", alternatively termed "memory", "puff up", or "Barus effect". This effect is usually described experimentally in terms of the swelling ratio (d/D) which is the ratio of extrudate diameter over the die diameter. The reasons for increased interest in this behaviour are numerous ranging from the desire to define the viscoelastic response of polymeric systems to the need to obtain direct relations between die swell and such polymer processing characteristics as swell in bottle blowing, thickness in extruded wire and cable insulation , "neck-in" in sheet extrusion, etc.

In spite of the importance of extrusion in polymer processing, there has not been much progress in relating die swell to the structure of the polymer.

It should be remembered that even non-elastic fluids will emerge from a capillary with a diameter different from that of the tube itself. Experiments indicated that for such non-elastic liquids at low Reynold's number, the emergent stream will exhibit a die swell (d/D) of about 1.10. For high Reynold's number flow, the emergent stream contracts giving a value (d/D) of about 0.87. There is a smooth transition between the two extreme limits, however, this effect is small compared to the large die swell observed with viscoelastic polymer melts.

Much effort has been devoted to find the expressions for polymer swell from a long capillary, assuming the capillary long enough, such that the effect of capillary length is excluded.

However, it has been observed that die swell greatly depends on the capillary dimensions. It is found that the swelling ratio decays exponentially with L/D (Figure 1.2). Although some work has been done to investigate the phenomenon, the explanation still remains unclear. The objectives of this project are:

1) To investigate the effect of capillary length on die swell for some types of commercial polymers low and high density polyethylene, polypropylene, polystyrene.

2) To examine the effects of extrusion variables, shear stress, shear rate, temperature, etc. on die swell phenomenon.



II LITERATURE SURVEY

2.1 Experimental Observations

With the rapid growth of the polymer processing industry, the importance of die swell becomes evident. One area in which die swell investigations have proven useful is in the field of bottle blowing of thermoplastic materials. Wechsler and Bayliss⁽³⁶⁾ investigated the effect of die swell in this flow molding process. In extending this work, Beynon and Glyde⁽⁷⁾ studied (d/D) as a function of shear rate and found that(d/D)increased with shear rate up to the critical rate at which certain flow defects appeared. At this point (d/D) went through a maximum and then decreased. One problem in determining (d/D) at high output rate arises because extrudate distortion makes it difficult or impossible to measure extrudate diameter, but experimentally the distortion can be minimized by using tapered dies. Beynon and Glyde⁽⁷⁾ agreed with Dillon and Johnston⁽¹³⁾ that the swell did decrease with increasing temperature, but the maximum attainable swell also increased with temperature.

The importance of die swell as a variable in the extrusion blowing of polyethylene bottles is also discussed by Wilson⁽³⁷⁾ who noted that die swell tends to increase the diameter and depends on the extrusion rate, die design, and polymer composition.

Burgess and Lewis⁽¹⁰⁾discussed the importance of die swell in die design, and noted that the actual amount of swell depended on the melt index of the polymer, the temperature and rate of extrusion, and die length, agreeing with others that the higher the temperature and the longer the die land the lower the swell, and the higher

the molecular weight the higher the swell. Actually, both melt index and die swell are complex functions of molecular weight, molecular weight distribution and branching. Thus a correlation between die swell and melt index may, in fact, be misleading. In the case of certain polymers, the generalizations given above may not be valid. In polyvinylchloride the degree of swell decreases with increasing molecular weight at a given shear rate⁽²⁹⁾.

In the pass years, several fundamental investigations were made and these are described briefly below. According to Goren, Middleman , and Gavis⁽¹⁶⁾swelling of jets of viscoelastic fluid might be due to relaxation of axial stresses.

Sieglaff⁽²⁹⁾ measured and correlated the effect of die geometry and polymer molecular weight on the post-extrusion of Polyvinylchloride resins but the experiments did not elucidate a mechanism.

Along with experimental data on die swell in polymer melts, Arai and Aoyama⁽¹⁾ discussed die wall restriction on the elastic shear deformation in steady flow. The shear modulus in steady flow must be a function of elastic shear stress, and the modulus increases with the molecular weight.

Huseby and Gogos⁽¹⁹⁾pointed out that when recoverable strain in tube flow is plotted versus swelling ratio, the resulting curves are consistent with the observation that swelling ratio is an increasing function of normal stress.

Kruse⁽²¹⁾ measured extrudate swelling for polypropylene (mol. wt. 540,000) in a N_2 -pressurized rheometer at 400^oF. The amount of swelling decreased with residence time in the die.

Bagley, Storey, and West⁽⁵⁾also pointed out in their experiments with polyethylene that (d/D) depends, at constant pseudo shear rate, on the length-to-radius ratio of the capillary even though the viscosity does not.

2.2 Some Proposed Mechanisms for Die Swell

Spencer and Dillon⁽³¹⁾ considered the orientation relaxation of polymer molecules on leaving the die as a major factor in the swelling phenomenon. Clegg⁽¹¹⁾ has disqualified this by stressing the necessity of comparing die transit time with relaxation time.

Metzner⁽²⁵⁾has derived an expression for the expansion ratio (d/D), that contains both axial and radial normal stresses.

In 1966, Nakajima and Shida⁽²⁷⁾ emphasized that elastic recovery is the most important factor in the swelling process in polymer melts. They derived an equation using the concept of rubber elasticity to calculate the tensile stress for the elastic deformation of the extrudate until its diameter becomes that of the capillary.

Following the analysis of Nakajima and Shida⁽²⁷⁾, Bagley and Duffey⁽³⁾ obtained an expression using a one-constant stored energy function for a Mooney material⁽²⁶⁾.

Bagley and Duffey⁽³⁾ also carried out an energy balance analysis along Graessley's lines⁽¹⁷⁾ and arrived at another equation.

Graessley, Glasscock and Crawley⁽¹⁷⁾assumed that the increase in the diameter of the extrudate is due to the release of elastic energy stored in the fluid inside the capillary. They introduced a modulus of elasticity estimated from the theory of rubber elasticity in terms of the average molecular weight between entanglements. Recently Tanner⁽³²⁾has proposed another expression relating recoverable shear at the wall to the swelling ratio based on the elastic recovery concept of a Poiseuille flow of a BKZ fluid. The BKZ fluid obeys the constitutive equation postulated by Bernstein, Kearsley and Zapas⁽⁶⁾. This constitutive equation is one of the integral type representations which can take the strain history into account.

To explain the effect of <u>die dimensions</u> on die swell of extruded (4) polymers, Bagley proposed that the swell is considered as the unretarded recovery of elastic strain imparted to polymer by two parts:

- a) Elastic deformation at the entrance
- b) Elastic deformation during shearing flow through the die due to the steady normal stresses

In long land die (e.g. large L/D capillaries) the entrance strain decays along the length of the die, and the die swell may be viewed as a consequence of the deformation due to normal stress generated in the shearing field. In a very short die the entrance deformation predominates.

The decay of swelling with capillary length might be expected to be a typical relaxation process, showing an exponential dependence on the time of transit through the die. If B is defined as the ratio of extrudate diameter to die diameter and t_a is the average time of transit through the die, then Bagley⁽⁵⁾ proposed the following decaying equation:

 $(B-B_{\infty}) = (B_0-B_{\infty}) \exp(-kt_a)$ (2.1) where B_0 and B_{∞} are values of B at zero and infinite transit times respectively and k is a decay rate constant.

Kawasaki, Tat Susaka and Ono⁽²⁰⁾ in a recent paper, considered the extruding process as a series of deformation mechanisms</sup>

1) Elongation from the reservoir to the entrance of the capillary

- The release of inner stress proceeding under a constant elongation
- 3) Recovery of remaining strain after leaving the capillary

Next, an Oldroyd model (series of a dash pots (μ_1) and Voigt elements $(\mu_2 \text{ and } G_2)$)are employed as the representative rheological model for molten polymers. This led them to an equation presenting die swell as function of polymer characteristics and die dimensions.

$$\log\left\{1 - \frac{1}{(B-\Delta)^2}\right\} = -\log\left\{\frac{\gamma(t_1)}{\gamma_2(t_1)}\right\} - \frac{1.74}{\dot{\gamma}_a^{\tau}}\left(\frac{L}{R}\right)$$

in which $\tau = \frac{\mu_1 + \mu_2}{G_2}$, $\dot{\gamma}_a$ is pseudo shear rate, B is die swell index $\left(\frac{d}{D}\right)$, Δ is die swell index of infinitely long capilary.

By varying the capillary length (L/R) while fixing the apparent shear rate $\dot{\gamma}_a$, a linear relation exits between $\log \left\{ 1 - \frac{1}{(B-\Delta)^2} \right\}$ versus (L/R).

III THEORETICAL BACKGROUND

3.1 Expressions Predicting Die Swell

Several expressions have been proposed for the prediction of die swell, centered on the concept of elastic recovery of the swelling process. These expressions relate the swelling ratio (d/D) to the recoverable shear (σ) .

The recoverable shear strain is usually defined from Hooke's law which seems to hold for most polymers:

 $\sigma = \tau_{12} J_o$ (3.1) where τ_{12} is the shear stress and J_o the shear compliance $(J_o = 1/G_o)$ where G_ is the shear modulus).

Coleman and Markovitz have shown that:

 $\tau_{11} - \tau_{22} = 2J_0 \tau_{12}^2$ (3.2)

where τ_{11} and τ_{22} are the first and second normal stress respectively. From Equation (3.1) and (3.2)

$$\frac{\tau_{11} - \tau_{22}}{2\tau_{12}} = \sigma$$
(3.3)

This expression led some authors to the definition of σ as "Stress Ratio".

Nakajima and Shida⁽²⁷⁾ used the concepts of rubber elasticity. They assumed that the polymer, in a capillary, is in an elongated state in the direction of the capillary axis. Consequently, the polymer in the capillary has the elastic energy in the same sense as the potential energy of a stretched spring. This energy will recover after passing through the capillary and this causes the die swell.

Assuming the molecular network of polymer is a Gaussian one $\binom{(22)}{}$, Nakajima and Shida calculated the tensile stress for the elastic deformation of the extrudate until its diameter becomes that of the capillary:

$$\frac{\tau_t}{NakT} = (\lambda - \lambda^{-2})$$
(3.4)

where $\lambda = (d/D)^2$, τ_t is the tensile stress, Na & k are the number of chains per unit volume, and Boltzmann's constant respectively.

Elastic modulus G_o, is given ⁽³⁵⁾

$$G_{o} = NakT$$
(3.5)

Therefore, τ_t has a meaning of tensile strain. Here Nakajima NakI

made a bold assumption that the tensile strain is taken as the quanlitative expression for the recoverable strain in the flow:

$$\overline{\sigma} = \frac{\mathbf{r}_{t}}{\operatorname{Nak}_{T}} = \left(\frac{\mathrm{d}}{\mathrm{D}}\right)^{2} - \left(\frac{\mathrm{d}}{\mathrm{D}}\right)^{-4}$$
(3.6)

Assuming the parabolic velocity profile, it has been shown⁽²²⁾that: $\sigma_{\rm w} = \sqrt{3} \ \overline{\sigma}$ (3.7)

. In case of a flat velocity profile:

$$\sigma_{W} = \sqrt{2} \ \overline{\sigma} \tag{3.8}$$

in which $\overline{\sigma}$ and σ_w are the average recoverable shear strain and at the wall respectively. If the parabolic velocity profile is assumed then: $-(1, 2, (1)^{-4})$

$$\sigma_{W} = \sqrt{3} \left\{ \left(\frac{d}{D} \right)^{2} - \left(\frac{d}{D} \right)^{-4} \right\}$$
(3.9)

Bagley and Duffey³ followed the analysis of Nakajima⁽²⁷⁾ and used one constant stored energy function for a Mooney material⁽²⁶⁾.

$$\overline{W} = C_1(I_1 - 3)$$
 (3.10)

where I, is the first strain invariant and C, is a constant i.e.,

 $I_{1} = \lambda_{1}^{2} + \lambda_{2}^{2} + \lambda_{3}^{2}$ (3.11) $\lambda_{1}, \lambda_{2}, \lambda_{3} \text{ are the principal extension ratios which are given as:}$ $\lambda_{1} = \lambda$ (3.12)

$$\lambda_2 = \lambda_3 = \lambda^{-1/2} \tag{3.13}$$

then

$$W = C_1(\lambda^2 + (2/\lambda) - 3)$$
(3.14)

and force f_b which is defined as:

$$f_{b} = \frac{d\bar{w}}{d\lambda} = 2C_{1}(\lambda - \lambda^{-2})$$
(3.15)

The tensional stress t_{xx} acting on the cylinder in the final elongated state is then:

$$t_{xx} = \lambda f_b = 2C_1(\lambda^2 - \lambda^{-1})$$
 (3.16)

on the other hand (35)

$$G_0 = 2C_1$$
 (3.17)

therefore, assuming

$$\bar{\sigma} = t_{xx}^{G}$$
(3.18)

Bagley obtained the relation:

$$\bar{\sigma}^2 = \left(\frac{d}{D}\right)^4 - \left(\frac{d}{D}\right)^{-2}$$
(3.19)
Bagley and Duffey⁽¹⁹⁾ also carried out an energy balance analysis along
Graessley's⁽¹⁷⁾ lines. The strain energy function in shear inside the

capillary is given (26)

$$\overline{W}_{\text{shear}} = \frac{1}{2} G_0 \overline{\sigma}^2 \qquad (3.20)$$

in the elongational case, in passing from the unstrained material to the strained case the stored strain energy per unit volume is:

$$\overline{W}_{elongation} = \frac{1}{2} G(\lambda^2 + \frac{2}{\lambda} - 3) \qquad (3.21)$$

Since $\overline{W}_{elongation}$ must equal \overline{W}_{shear} at the die exit ,we obtain (for

$$\bar{\sigma}^2 = (d/D)^4 + 2/(d/D)^2 - 3$$

(3.22)

Another expression relating recoverable shear at the wall to the swelling ratio has been proposed by Tanner⁽³²⁾ based on the elastic recovery concept of a Poiseuille flow of BKZ fluid⁽⁶⁾.

He made the following assumptions:

- 1) The flow is isothermal and incompressible
- 2) The die is long enough
- 3) Inertial effects in the flow are ignored
- Gravity, other body forces, and surface tension forces are ignored
- 5) The flow at exit may be approximated by a sudden strain which takes the fluid from the viscometric stress state inside the tube instantaneously to the zero stress state outside the tube
- 6) As a constitutive equation, BKZ form" is assumed

On the basis of these assumptions, Tanner got the expression $\sigma_{w}^{2} = 2[(\frac{d}{D})^{6} - 1)] \qquad (3.23)$

Since (d/D) approaches a value of $1.10^{(17)}$ for slow Newtonian flow, Tanner suggested a modification to the previous equation

$$\sigma_{\rm w}^2 = 2[((\frac{d}{D}) - 0.1)^6 - 1]$$

An evaluation of the above equation predicting die swell has been (35) carried out by Vlachopoulos, Horie, and Lidorikis

3.2 Capillary Flow:

The three basic equations which describe the flow of a fluid in a capillary are the equations of continuity, momentum, and energy. The momentum equation in its most general form is:

$$\frac{DV}{Dt} = -\nabla P - \nabla \cdot \overline{t} + \Sigma \rho F \qquad (3.25)$$

In cylindrical co-ordinates (r, θ , z) Equation (3.25) may be represented in terms of τ , by the following equation. Assuming gravity to be the only field force present, so only z component is important.

(3.24)



z component:

$$\rho\left(\frac{\partial V_{z}}{\partial t} + \frac{V_{r}\partial V_{z}}{\partial r} + \frac{V_{\theta}}{r}\frac{\partial V_{z}}{\partial \theta} + \frac{V_{z}\partial V_{z}}{\partial z}\right) = -\frac{\partial P}{\partial z} - \left\{\frac{1}{r}\frac{\partial}{\partial r}(r_{r}\tau_{r}z) + \frac{1}{r}\frac{\partial \tau_{\theta}z}{\partial \theta} + \frac{\partial \tau_{\theta}z}{\partial \theta} + \frac{\partial \tau_{z}z}{\partial z}\right\} + \frac{\partial \tau_{z}z}{\partial z} + \rho_{g}z \qquad (3.26)$$

The following assumptions will be made for the capillary flow:

- 1) The flow is steady
- 2) The axial component of the velocity (V_z) is assumed to be a function of the radial distance (r) alone
- 3) There are no radial and tangential components of the velocity
- 4) There is no slippage at the wall
- 5) The tube is sufficiently long so that end effects are negligible
- 6) The fluid is incompressible
- 7) Isothermal conditions prevail throughout
- 8) Viscosity doesn't change appreciably with change in pressure down the tube

Then the Equation (3.26) reduces to

$$0 = -\frac{\partial P}{\partial z} - \frac{1}{r} \frac{\partial}{\partial r} (r\tau_{rz})$$
(3.27)

which becomes upon integration;

$$\tau_{rz} = -\frac{r}{2} \frac{\partial P}{\partial z}$$
(3.28)
At the wall, since $r = R$ and $\tau_{rz} = \tau_{w}$

$$\tau_{w} = -\frac{R}{2} \frac{dp}{dz}$$
(3.29)

From Equations (3.28) and (3.29)

$$\tau_{\mathbf{r}\mathbf{Z}} = \frac{\mathbf{r}}{\mathbf{R}} \frac{\tau}{\mathbf{w}} \tag{3.30}$$

For laminar steady flow through a capillary of radius R, the volume flow rate Q is given by the integral:

$$Q = 2\pi \int_{0}^{R} r V_{z}(r) dr$$

Using Equation (3.30) one gets:

$$Q = 2\pi \left(\frac{R}{\tau_w}\right)^2 \int_0^{\tau_w} \tau \frac{V_z d\tau_{rz}}{r z z z} d\tau_{rz}$$

(3.31)

The velocity can be given by

$$V_{z} = \int_{r}^{R} \left(-\frac{dV_{z}}{dr}\right) dr = \frac{R}{\tau_{w}} \int_{\tau}^{\tau_{w}} \left(-\frac{dV_{z}}{dr}\right) d\tau_{rz}$$
(3.32)

Combining Equation (3.31) and (3.32) gives:

$$\frac{4Q}{\pi R^3} = \frac{8}{\tau_w^3} \int_0^{\tau_w} \tau_{rz} \int_{\tau_{rz}}^{\tau_w} \left(-\frac{dV_z}{dr}\right) d\tau_{rz} d\tau_{rz}$$
(3.33)

Integrate by parts

$$\frac{4Q}{\pi R^3} = \frac{4}{\tau_w^3} \int_0^w \tau_{rz}^2 \left(-\frac{dV_z}{dr}\right) d\tau_{rz}$$
(3.34)

which is the general equation that relates the flow to the velocity gradient in the system.

* For a Newtonian fluid Equation (3.34) becomes:

$$\frac{4Q}{\pi R^3} = \frac{\tau_w}{u} = -\frac{R}{2\mu} \frac{dP}{dz}$$
(3.35)

This equation can be used to define a capillary shear diagram as $4Q/\pi R^3$ versus $\tau_{..}$. The term $4Q/\pi R^3$ is called "pseudo-shear rate".

A simple relation between the flow rate and the wall shear rate was obtained by Rabinowitsch differentiation of Equation (3.34)

$$\frac{d\left[\left(\tau_{w}^{3}\left(\frac{4Q}{\pi R^{3}}\right)\right]}{d\tau_{w}} = 4\tau_{w}^{2}\left(-\frac{dV_{z}}{dr}\right)_{w}$$
(3.36)

which results in:

$$\left(-\frac{dV_z}{dr}\right)_w = \frac{3}{4} \left(\frac{4Q}{\pi R^3}\right) + \frac{\tau_w}{4} - \frac{d(4Q/\pi R^3)}{d\tau_w}$$
(3.37)

This equation can be used directly to reduce the capillary shear diagram to the basic shear diagram as follows:

- 1) For a given value of $\tau_{_{\rm W}},$ the value of $4Q/\pi R^3$ can be obtained from the data
- 2) The stope of the curve can also be obtained at that point.
- 3) Thus $\left(-\frac{dV}{z}\right)$ is calculated from Equation (3.37)
- 4) Both τ_{W} and $\left(\frac{dV}{dr}\right)_{W}$ are measured at the same point and thus are

the terms of the basic diagram.

3.3 Errors in Capillary Flow:

3.3.1 End effects:

Equation (3.30) was derived from the assumption that there is no entrance and exit of the tube, however, the end effects cause an appreciable amount of pressure drop, the estimation of τ_w by Equation (3.30) is in error. One way to eliminate the entrance effect is to use large length-to-diameter ratio of the capillary to reduce the error but it is difficult to work with long capillaries.

An empirical method of correcting for entrance effects has been suggested by $Bagley^{(2)}$. The procedure developed by Bagley is outlined below.

Following Figure (3.2), P is the pressure gradient in the region of steady flow then:

$$P_{s} = \frac{\Delta P}{ND+L}$$
(3.38)

where ND, as shown by Figure(3.2), represents a fictitious tube length that, when added to the actual length, enables one to use the over-all pressure drop in calculating the gradient in the steady flow section.

The expression for the shear stress at the wall in the steady flow section of the tube can now be written:

$$\tau_{\rm W} = \frac{\rm D}{\rm 4} \left(\frac{\Delta \rm P}{\rm L + \rm N \rm D} \right)$$
(3.39)

)



 τ_{i} is a unique function of Γ , which is defined as:

$$\Gamma = \frac{4Q}{\pi R^3}$$

$$\tau = g(\Gamma)$$

Rearranging Equation (3.39) becomes:

$$\frac{L}{D} = -N + \frac{\Delta P}{4g(\Gamma)}$$

N: is the total end correction.

Equation (3.40) suggests that the value of N might be determined from flow measurements made with a series of capillary tubes having different L/D ratios. For each tube, the pressure drop ΔP giving some specific value of pseudo shear rate would be determined. Then, by plotting (L/D) versus ΔP , a straight line having -N as an intercept would be obtained. The corrected value of τ_{i} will be calculated from (3.39).

3.3.2 Slip at the Wall

The derivation of Equation (3.30) is based on the assumption that velocity is zero at the wall of the capillary. Brodkey has shown that a plot of $4Q/\pi R^3$ versus τ_w will determine the existence or absence of slip. For a system with slip, $4Q/\pi R^3$ must decrease at constant τ_w , with increasing diameter of the capillary. It is often found that in the flow of molten polymers, a no-slip condition can be assumed.⁽⁹⁾ 3.3,3 Heat Effects

It is assumed that the flow is in isothermal condition. Gerrard and Appledoorn⁽¹⁵⁾have shown that the use of an average temperature is unimportant as it is insensitive to changes that can occur because of temperature gradient. Lidorikis⁽²³⁾has shown that heat effect is negligible under the usual operating conditions of viscometer.

(3.40)

IV EXPERIMENTAL PROCEDURE

4.1 Equipment

The experiment was carried out by using the Instron capillary rheometer model 3211.

The model 3211 Rheometer has a synchronous motor and gearbox which drives the plunger at a constant rate, independent of load on the plunger. Thus, the volumetric flow rate through the capillary will be constant, making it unnecessary to collect extrudate, weigh it and back - calculate through the density to obtain the volumetric rate of flow.

The push button drive system of the 3211 Rheometer makes it simple to instantaneously select from six shear rates (plunger speeds) for testing a single load of material in the barrel. The maximum and minimum shear rates span a 333:1 range with a given capillary, and the plunger speeds are adjustable from 20 inches/minute to 0.006 inches/ minute by means of changing gears.

Since the viscosity of many materials is extremely temperature dependent, the model 3211 Rheometer is designed to control absolute temperature within $\pm 1^{\circ}$ C and the temperature profile from the top to the bottom of the rheometer barrel can be controlled to within $\pm 2^{\circ}$ C.

To investigate the effect of capillary dimensions on die swell, nine capillaries were used, most capillaries are made of brass, all have the entry angle of 90 degrees. The length to diameter ratios of these capillaries vary from zero to twenty five. Table(4-1) gives the specifications of these capillaries.

TABLE OF CAPILLARIES USED

NO.	MATERIAL	ENTRANCE	DIAMETER	LENGTH	L/D
		ANGLE	(INCHES)	(INCHES)	
1	Brass	900	0.0525	1.300	24,8
2	Brass	900	0.0525	1.050	20.0
3	Brass	9 0 °	0.0525	.839	16.0
4	Brass	900	0.0525	.519	9.9
5	Brass	90°	0.0525	. 418	7.9
6	Stainless Steel	90°	0.0525	.281	5.01
7	Brass	900-	0.0525	.157	2.99
8	Stainless Steel	90°	0.0525	.0517	0.99
9	Brass	900	0.0525	≈ °	220

Table 4.1

4.2 System Operation:

The material to be tested is loaded into the extrusion barrel, allowed to come up to temperature and is forced, at constant speed, through the capillary. The plunger forces, corresponding to selected plunger speeds, are indicated on a recorded paper. The forces and corresponding plunger speeds can be converted to shear stress and shear rate by a simple mathematical calculation involving the geometry of the barrel and capillary as discussed in Section (4.4).

4.3 Materials

The commercial samples of four polymers are used to make the investigation:

- (1) Low density (Branched) polyethylene (Union Carbide Canada Limited)
- (2) High density (Linear) polyethylene (Union Carbide Canada Limited)
- (3) Polypropylene (Shell Canada Limited)

)

- (4) Commercial Polystyrene (Monsanto Company, Limited)
- (5) Standard Polystyrene (Pressure Chemical Company, Pittsburgh Pa.)

The blent polystyrene was prepared by mixing and dissolving the narrow distribution polystyrene in tetrahydrofurane (at room temperature), then precipitating and filtering with purified methanol, and evaporating the remaining in a vacuum oven.

The average molecular weight of blent polymer is calculated from the following equations:

$$\bar{M}_{w} = \Sigma W_{i} (M_{w})_{i} / \Sigma W_{i}$$
$$\bar{M}_{n} = \Sigma W_{i} / \Sigma (W_{i} / (\bar{M}_{ni}))$$

$$\bar{\mathbf{M}}_{z} = \frac{\sum_{i}^{\sum W_{i}} \overline{\mathbf{M}}_{wi}^{2}}{\sum_{i}^{\sum W_{i}} \overline{\mathbf{M}}_{wi}}$$
$$\bar{\mathbf{M}}_{z+1} = \frac{\sum_{i}^{\sum W_{i}} \overline{\mathbf{M}}_{wi}^{3}}{\sum_{i}^{\sum W_{i}} \overline{\mathbf{M}}_{wi}^{2}}$$

POLYMER SAMPLES USED

TRADE NAME	м_w*	M _w /M _n *	POLYMER	SUPPLIER
DFDY-0701 DFDQ-0118 DFDY-6005	51,300 53,500 82,800	3.72 3.00 3.96	L.D.Polyethylene L.D.Polyethylene L.D.Polyethylene	Union Carbide Canada, Ltd.
DMDA - 7930	69,590	4.17	H.D.Polyethylene	Union Carbide Canada, Ltd.
PP-5820	287,000		Polypropylene	Shell Canada Ltd.
LUSTREX HF-55 LUSTREX HT 42.1	320,000	3.10	Polystyrene	Monsanto Company, Limited
BLENT POLYSTYRENE (mixing two standard Polystyrenes, one having M _w =1,800,000	498,000	2.21	Polystyrene	Pressure Chemical Company

 $\frac{\bar{M}_{w}}{\bar{M}_{n}} \leq 1.2$

and another having $\bar{M}_w = 200,000$

 $\frac{\bar{M}_{w}}{\bar{M}_{n}}$ = 1.06) BLENT POLYSTYRENE having $\bar{M}_{z}\bar{M}_{z+1}/\bar{M}_{w}^{2}$ = 11.04

* Determined by Suppliers

TABLE 4-2

4.4 Treatment of Data

4.4.1 Shear Diagram

The calculation of basic shear diagram in capillary rheometer requires the measurements of volumetric flow rate and the pressure drops through the capillary. Shear stress and shear rate at the wall are obtained as follows:

- 1) From the volumetric flow rates, pseudo shear rate $(4Q/\pi R^3)$ is obtained.
- At a value of pseudo shear rate, the corresponding pressure is obtained and cross plotted versus the L/D ratio (Fig. 4.1)
- 3) The intersections of these lines with x-axis are used to calculate the corrected shear stresses.
- 4) From the plot of corrected shear stress versus pseudo shear rate (Fig. 4.2), the slope is obtained, thus $-dV_z/dr$ (= $\mathring{\gamma}_w$) is calculated by using Rabinowitsh Equation (Eq. 3.37)

5) The plot of $\dot{\gamma}_{W}$ versus τ_{W} gives the basic shear diagram (Fig. 4.3) Value of Pressure, $40/\pi R^2$, τ_{W} , $\dot{\gamma}_{W}$ and swelling ratio for all polymers are given in Appendix I.

4.4.2 Melt Fracture

The incipience of melt fracture was determined visually by the appearance of a pronounced distortion in the extrudate. This was fairly easy for most polymer samples. The Instron capillary rheometer is equipped with a chart recorder. At the incipience of melt fracture, the chart records a zig-zag line, however, the best way to recognize the on-set of melt fracture is by observing the extrudate distortion.








4.4.3 Extrudate Swelling

The diameter of the extrudate was obtained by extruding the polymer melt downward directly into the air. All experiments were made in this manner, and the diameter of hardened extrudate was measured with a micrometer to the nearest 0.001 inch.

To obtain a specimen for measurement the extruding molten rod was first cut short at the capillary. As fresh extrudate emerged, it cooled and hardened in the first few inches beyond the exit The diameter of the extrudate decreases because of elongation at the exit from the increasing weight of the extrudate. All diameter measurements were made approximately 1/4 inch back from the leading end where elongation was negligible. The extrudate was quite uniform in diameter at low shear stresses but lost their uniformity at the critical stresses due to the extrudate distortion.

All the diameters of extrudates have been corrected for the density difference between room temperature and extrusion temperature

$$\frac{d}{d_o} = (\rho_o/\rho)^{1/2}$$

3

where d = swelled diameter of melt at extrusion temperature
 d = swelled diameter of frozen polymer
 p* = density of melt, p* density of frozen polymer

4.4.4. Molten Polymers Behave as a Power Law Fluid

Logarithmic flow curves of molten polymers often appear to be straight if restricted to one or two decates of shear rate, but when extended over several decades, they are usually not straight.

* Value of density is taken from reference source (25)

Logarithmic plots of shear rate versus shear stress for investigated polymers are shown in Figure (4.5.) It is observed that low density polyethylene, in the range of experimental data, follows the power-law fluid ($\tau = KG^n$) with n in the range of 0.4-0.5

The flow curves of high density polyethylene, polypropylene, and especially polystyrene somewhat deviate from power law. This deviation is what we would expect because molten polymer is viscoelastic material, its rheological equation is not exactly represented by the power law, every rheological model contains at least two parameters, one for viscosity and the other for elasticity characteristics.









V RESULTS

5.1 Reproducibility

The measurements of extrudate diameters were repeated four times to check the reproducibility of these values. The applied pressures are obtained within 2% while the diameter of the extrudate was found reproducible within nearly 1 %. All measurements are taken in a standard way, in this way while the absolute diameter of the extrudate might be in doubt because of "frozen-in" mechanism but comparison between those values of different capillaries does make sense. It was observed that down drawing by weight does not affect the measurement of extrudate diameter, because the measurement is made at 1/4" from the leading end.

5.2 Effect of Temperature on Die Swell

Figure (5-1) is the plot of die swell(d/D) vs. true shear stress for low density polyethylene at four different temperatures ranging from 150°C to 210°C. It is found that swell is independent of temperature over this range. This agrees with Graessley ⁽¹⁷⁾ and Smelkov⁽³⁰⁾ for Polystyrene and PMMA. This result, however, disagrees with Horie⁽²²⁾. Horie found that at a fixed true shear stress, die swell increases with temperature for low density polyethylene.

Investigating the effect of temperature on die swell of polystyrene, PMMA, Low density polyethylene, Horie⁽²²⁾made the following conclusions:

- At a fixed shear rate, die swell decreases with temperature for polystyrene and PMMA.
- At a fixed shear rate, die swell increases with temperature for low density polyethylene.

Conclusion (1) is in agreement with Beynon and Glyde⁽⁷⁾, Brydson⁽⁹⁾, Dillon and Johnston⁽¹³⁾. Conclusion (2) disagrees with Beynon and Glyde⁽⁷⁾ and Dillon and Johnston⁽¹³⁾. Unfortunately, the reasons for the rather unconventional behaviour of these materials are not clear.



5.3 Effects of Shear Rate and Shear Stress on Die Swell

Figures (5.2.1 to 5.2.4) are the plots of die swell versus shear stress with different capillaries for all polymers studied.

The following conclusions could be drawn:

1) With a fixed capillary, die swell increases with shear stress for low, high density polyethylene, polypropylene

2) With a fixed capillary, die swell increases with shear rate for low, high density polyethylene, polypropylene, polystyrene These results are definitely in agreement with Horie⁽²²⁾ and with the bulk of literature^{(7),(29)}.

It should be mentioned that extrudate swelling is only investigated up to critical stress, beyond that limit, measurements are impossible to carry on due to the zig-zag shape of extrudate. McInstosh⁽²⁴⁾ found that the plot of die swell versus shear stress increases to a maximum value then decreases beyond the critical shear stress.

5.4 Effect of Molecular Weight Distribution

The effect of molecular weight distribution on die swell has been carefully investigated by many former researchers (17),(22). The general









conclusion is: Die swell increases with molecular weight distribution which is represented by the factor ($\overline{M}_{z}M_{z+1}/\overline{M}_{w}^{2}$).

In Figure (5.3) the plot of swelling ratio versus true shear stress for low density polyethylene with various polydispersity $(\bar{M}_{w}/\bar{M}_{p})$ is shown.

Dependence on factor $\overline{M}_{z} \overline{M}_{z+1} / \overline{M}_{w}^{2}$ implies that die swell is influenced by high molecular weight tail.

In Section (3.1), it has been stated that the swelling ratio (d/D) is a function of recoverable shear, and the recoverable shear is defined from Hooke's law in shear:

$$\sigma = \tau_{12} J_{0}$$
(5.1)

where J_o is the shear compliance of material. Graessley and co-workers⁽¹⁷⁾ carried out rheogoniometer measurements on concentrated solutions and melts of polvstyrene and developed the following correlation between "true" and Rouse shear compliance at zero shear rate:

$$J_{o} = \frac{2.2 \times J_{R}}{1 + 0.347 \rho E_{o}}$$
(5.2)

where J_R is the Rouse shear compliance

$$J_{R} = \frac{2}{5} \frac{\bar{M}_{Z}\bar{M}_{Z}+1}{\bar{M}_{W}^{2}} \frac{\bar{M}_{W}}{\rho R_{g}T}$$
(5.3)

 $E_{o} = \frac{M}{W}/16,000$ is the entanglement density at zero shear, ρ is the density, R_{σ} is the ideal gas constant.

It is clear that shear compliance (J_0) is related to the molecular weight distribution $(\tilde{M}_z \tilde{M}_{z+1}/\tilde{M}_w^2)$ through the Rouse shear compliance. That is the reason why the molecular weight distribution has great importance in polymer swell.



High density polyethylene which has linear chain molecules is compared with low density polyethylene (branched molecules), Figure (5.3). It can be concluded that: branched polyethylenes are less swelling than linear polyethylenes with similar molecular weight\$ distributions.

This is in agreement with Horie⁽²²⁾as well as Bengou and Glyde⁽⁷⁾ 5.5 Effect of Die Length on Swelling Ratio

The effect of die length on swelling ratio is investigated for low and high density polyethylene, polypropylene and polystyrene.

Figures (5.4 to 5.10) are plots of die swell versus L/D for different polymers. It is observed that low density polyethylene needs a long capillary to level off, in our data the swelling ratio seems still decreasing at the value of L/D equal 24.8. Die swell of high density polyethylene reaches equilibrium value relatively faster (L/D=15), the same behaviour is noticed for polypropylene and polystyrene which level off at L/D equal 15 and 12 respectively.

It should be recalled that high density polyethylene, polypropylene and polystyrene are linear polymers while low density polyethylene is a branched polymer. The equilibrium values change with different shear rates. These results are generally in agreement with $Graessley^{(17)}$ (Polystyrene) and $Bagley^{(5)}$ (Polyethylene)











VI ANALYSIS

6.1 Bagley's Suggestion

It was suggested by Bagley⁽⁵⁾(Section 2.2) that swelling of an extrudate decays exponentially with the shear strain put on the melt system. Bagley fitted his data to his suggested Equation (2.1) by a least-squares method:

$$(B-B_{\infty}) = (B_{0}-B_{\infty}) \exp(-kt_{a})$$
 (2.1)

His most interesting relationship is the plot of k versus shear rate results in a straight line passing through the origin, so the following relationship can be written:

$$k = (c/4)G$$
 (6.1)

If Q is the output rate through a capillary of radius R and length L then:

$$t_a = \pi R^2 L/Q \tag{6.2}$$

which may be written as:

$$t = 4(\pi R^3/4Q)(L/R)$$
 (6.3)

or

$$t_{2} = 4(L/R)/G$$
 (6.4)

where G is the pseudo shear rate. Combine Equation (6.1), (6.4) with Equation (2.1), we obtain:

$$(B-B_{m}) = (B_{m}-B_{m}) \exp(-c L/R)$$
 (6.5)

c is called the decay rate of swelling with die length being independent of shear rate, shear stress or residence time, so c depends only on the kind of polymer used. Equation (6.5) suggested by Bagley is used to fit data for five polymers studied: high and low density polyethylene, polypropylene, and polystyrene. The curves are shown from Figure (6.1) to (6.4) and the parameters are tabulated in the following tables.

TABLE 6.1

Parameters of Equation (6.5) found at $150^{\circ}C$ for Low Density polyethylene (0701) $\overline{M}_{w} = 51,000$, $\overline{M}_{w}/\overline{M}_{n} = 3.72$, $T = 150^{\circ}C$

LOW DENSITY POLYETHYLENE (0701)

$G(Sec^{-1})$ $\tau_w(dynes/cm^2x10^{-5})$ $\dot{\gamma}_w(Sec^{-1})$	3.8 1.36 3.8	12.8 2.80 17.0	38.6 4.52 51.8	128 7.40 173.1
(*) Bo	1.985	2.299	2.529	2.735
(**) ^B ∞	1.36	1.46	1.54	1.65
C	.14	.20	.19	.22

TABLE 6.2

LOW DENSITY POLYTHYLENE (0118) $\overline{M}_{w} = 53,500 \quad \overline{M}_{w}/\overline{M}_{n} = 3.00 \quad T = 150^{\circ}C$

$G(Sec^{-1})$ $\tau_w(dynes/cm^2 \times 10^{-5})$ $\dot{\gamma}_w(Sec^{-1})$	3.8 1.8 4.48	12.8 3.14 16.47	38.6 5.09 53.42	128 8.08 173.56
B(*)	1.891	2.254	2.546	2.799
(**) B _∞	1.37	1.43	1.49	1.58
c	.200	.233	.224	.251

(*) Value obtained by regression

(**) Value obtained from experimental data

TABLE 6.3

HIGH	DENSITY POLYETHYLENE	(7930)	$\bar{M}_{w} = 69,590$	$\bar{M}_{w}/\bar{M}_{n} =$	4.17 $T = 150^{\circ}C$
	$G(Sec^{-1})$ $\tau_w(dynes/cm^2 x 10^{-5})$	3.8 1.11	12.8 2.54	38.6 4.97	128 9.13
	Ÿ _w (Sec ^{−1})	3.89	14.92	45.97	161.21
. [в (*) °	1.804	1.986	2.325	2.850
	B∞ ^(**)	1.367	1.492	1.618	1.777
	c	.239	.284	.302	.280

TABLE 6.4

POLYPROPYLENE (PP.5820) \overline{M}_{1} = 287,000 T = 180°C

	W				Construction of the second second second second second
$G(Sec^{-1})$ T x 10 W (dynes)	3.86 $(cm^2)^{83}$	12.8	38.6	128 4.76	
γ _w (Sec ⁻¹)	4.51	16.5	41.6	144.25	
(*) B _o	1.531	1.804	2.252	2.751	(cal.)
(**) ^B ∞	1.304	1.458	1.572	1.804	
с	0.306	0.350	0.311	0.281	

TABLE 6.5

POLYSTYRENE: (HF.55)

T=170°C		$\bar{M}_{w} = 320,000$	÷	$\bar{M}_{w}/\bar{M}_{n} = 3.1$
G(Sec ⁻¹)	5.8	19.38		58
$\tau_{\rm w}$ x10 ⁻⁵ (dyn	es.05	5.09	-	7.31
Ŷ _w (Sec ^{-⊥})	5.8	28.35		84.07
. B (*) o	1.570	1.859	l e	2.220
(**) ^B ∞	1.302	1.454		1.612
c	0.415	0.357		0.261

(*) Value obtained by regression

(**) Value obtained from experimental data.







--2.



Fig. (6.4) Fitting of Bagley's decaying equation (6-5) for Polystyrene

POLYSTYRENE: (HT 42.1)		$T = 170^{\circ}C$	- 	
	$G(Sec^{-1})$ $\tau_{w} \times 10^{-5} (dynes/cm^{2})$	5.8 4.49	19.38 6.99	58. 9.30
	Υ _w (Sec ¹)	7.54	27.03	98.77
	во	1.654	1.895	2.255
	B∞	1.319	1.436	1.592
	C	0.569	0.330	0.300

TABLE 6.6

The decay equation suggested by Bagley seems to fit our data very well for most of polymers studied, however, there are some pitfalls of significant importance.

- 1) The decay rate is not constant with respect to pseudo shear rate (Table 6.1 to 6.6). For some polymers, decay rate could be considered constant within experimental error, while in the case of polystyrene, it could hardly be constant but decreases with pseudo shear rate.
- 2) If the stored energy is dissipated along the capillary then this energy must convert to heat which changes the viscosity of the polymers. However, the apparent viscosity does not change, this is demonstrated by the straight line of the plot pressure versus die length.

Our future work could be more devoted to investigate the possibility of this dissipated energy.

Equation(6.5) suggested by Bagley would be useful in practical purpose when the equation parameters B , B_0 , c could be related

to the material properties and processing conditions. In future work, it would be worthwhile to investigate this relationship.

It is clear that the plot of die swell index, d/D, versus L/D decays exponentially, however, this shape of the curve could be fitted by many forms of equation. Accordingly, we do not have any fundamental equations at hand. Bagley's equation should be regarded only as a curve fitting at experimental data.

6.2 Effect of Deborah Number on Die Swell

6.2.1 Time Constant

The time constant of a material is defined in many ways in the literature. It may be defined for a particular theory such as the theories of $\text{Rouse}^{(28)}$ and $\text{Graessley}^{(15)}$. It also may be defined as the inverse of the shear rate at which the viscosity decreases to some fixed percentage of the zero - shear rate viscosity. The following table summarizes all common definitions for time constant.

TABLE 6.2.1

Time	constant	Where found	Remarks
	θ _x	Harris ⁽¹⁸⁾	x represents viscosity (μ), or dynamic viscosity (μ). For definition see Figure (6.5)
	Θ	Work by Graessley and co-workers	<pre>16b) Defined in Graessley's theory and is obtained by superimposing viscosity data on a master curve for viscosity versus shear rate.</pre>

θ _R	Rouse ⁽²⁸⁾	$\begin{split} &\theta_R = \frac{6\mu_o M}{\Pi^2 CRT} & \text{defines the longest or} \\ &\text{largest time constant in the Rouse} \\ &\text{theory good only for dilute solutions.} \\ &\text{No "power law" region defined in} \\ &\text{this theory. The time constant is} \\ &\text{the same as that used by Bueche} \\ &\text{except for a constant multiple of 2.} \end{split}$
Θ _T	(34) Tobolsky and co-workers	Obtained from stress relation work by Procedure X as described in work by Tobolsky and Murakami
Θ _N	Graessley and co- workers (16b)	Obtained from a modification of (38) Williams' work on dilute solutions .
Θ _w	work by (38) M.C.Williams	Obtained from Williams' theory for intermediately concentrated solutions. $\Theta_{\rm W}$ is proportional to $\frac{\mu_{\rm O}}{c^2}$

Harris ⁽¹⁸⁾, working with solution of polystyrene at 25°C found that it is possible to relate the time constant θ_{μ} and θ_{μ} 'to concentration and molecular weight for one and two components (blends) system.

 $\Theta_{\mu} = 4.0 \times 10^{-16} \text{ c}^{3.77} \text{ M}_{w}^{3.27}$ $\Theta_{\mu} = 4.16 \times 10^{-15} \text{ c}^{2.63} \text{ M}_{w}^{2.92}$

where $M_{\rm w}$ and C are the weight average and polymer concentration.

Tobolsky found that for polymers having a narrow distribution of molecular weight $\theta_{\rm T}$ varies with 3.5 power of the molecular weight.



ine and

6.2.2 Definition of Deborah number

Deborah number is defined (25) as the ratio of the natural time of the material to the duration time of a process:

$$N_{\text{Deb}} = \frac{\Theta}{\Theta_{t}}$$
 (time constant of the material)

Metzner⁽²⁵⁾used Tobolsky time constant to define Deborah number. Processing time (θ_t) is used as the average residence time required for a particle of material to flow through the capillary which is:

$$\Theta_{t} = \frac{\pi R^{2} L}{Q} \quad (Sec)$$

According to the definition of pseudo shear rate (G)

$$G = \frac{40}{\pi R^3}$$

hence:

$$\Theta_{t} = \frac{8}{G}(\frac{L}{D})$$

This definition of processing time has also been used by Bagley⁽⁵⁾, Metzner⁽²⁵⁾ and Roger⁽²⁸⁾ in investigating the effect of capillary dimensions on die swell. Processing time is also designated as t_a .

6.2.3 Effect of Deborah Number on Polymer Processing

Metzner⁽²⁵⁾et al. has stressed the importance of this number on the extrusion of polymer melt through a capillary. If the Deborah number is large i.e. if the time span of the fluid memory exceeds the residence time in the tube, the emerging extrudate is able to recall its state prior to entry into the tube. Conversely, as this dimensionless ratio approaches zero, the extrudate is able to recall only the flow conditions in the tube. ⁽²⁵⁾However the relationship between Deborah number and die swell has not been proposed by former investigators.

To investigate the possible effect of processing time to die swell, the plots of die swell index, d/D, versus average residence time are shown in Figure (6.6) to Figure (6.9) for the polymers studied.

The following conclusions could be made from the plots:

- At a fixed pseudo shear rate, die swell decreases with residence time to a equilibrium value depending on pseudo shear rate.
- At a fixed residence time, die swell increases with pseudo shear rate.
- 3) The fact that all data points do not fall on the same curve means residence time or Deborah number is not the only factor determining die swell.

The importance of Deborah number as related to the phenomenon of die swell, is still unknown. Nevertheless, we can conclude that die swell is not solely dependent on the magnitude of this number.

6.3 <u>Relationship Between Recoverable Shear Strain of a Short and Long</u> <u>Capillary</u>

Hooke's law in shear is assumed to be obeyed by most of molten polymers

 $\sigma = J_0 \tau_{12} \tag{5.1}$

in which σ is the recoverable shear strain, stress and J the shear compliance (J = 1/G where G is the shear modulus).

Following the model suggested by Bagley (Section 3.1) which relates the average coverable shear, $\overline{\sigma}$, to the die swell (Equation 3.22)








$$\bar{\sigma} = \left[\left(\frac{d}{D} \right)^4 + \frac{2}{\left(\frac{d}{D} \right)^2} - 3 \right]^{1/2}$$

The relationship between average recoverable shear strain and its value at the wall has been derived in detail ⁽²²⁾. The following relation-ship would hold in the case a parabolic velocity profile is assumed:

$$\hat{\sigma}_{W} = \sqrt{3} \ \bar{\sigma} \tag{3.7}$$

In the case of very short capillary, a flat velocity profile is obtained, then the following relationship could be used (22)

$$\sigma_{\rm w} = \sqrt{2} \ \bar{\sigma} \tag{3.8}$$

Combining (3.22) and (3.7), then replacing $\mathbf{6}$ in (5.1) by $\mathbf{6}_{w}$ we would obtain:

$$\sigma_{W} = \sqrt{3} \left[\left(\frac{d}{D} \right)^{4} + \frac{2}{\left(\frac{d}{D} \right)^{2}} - 3 \right]^{1/2} = J_{o}^{\tau} W$$
(6.6)

It has been shown that (Section 4.4.4) in a short range of pseudo shear rate, molten polymer behaves as a power law fluid which means:

$$\tau_{w} \in KG^{n}$$
 (6.7)

Combining (6.6) and (6.7)

$$\sqrt{3} \left[\left(\frac{d}{D} \right)^4 + \frac{2}{\left(\frac{d}{D} \right)^2} - 3 \right]^{1/2} = J_0 KG^n$$
(6.8)

Taking logarithm of both sides

$$\log \left(\frac{d}{D}\right)^{4} + \frac{2}{\left(\frac{d}{D}\right)^{2}} - 3 \right|^{1/2} = n \log G + (\log J_{0}K - \log \sqrt{3}) (6.9)$$

According to Equation (6.9), the plot of
$$\left(\frac{d}{D}\right)^{4} + \frac{2}{\left(\frac{d}{D}\right)^{2}} - 3 \right|^{1/2} = \overline{\sigma}$$

versus G on logarithmic paper would give a straight line with slope n.

66

(3.22)







Ó

for Polypropylene





Figures (6.10) to (6.13) are the plots of $\overline{\mathfrak{G}_{\mathcal{P}}}$ studied.

It appears that the plots do give the straight lines particularly for long capillaries (long enough to obtain a die swell index, d/D, at equilibrium value).

The values of the slopes of the plots $\overline{\mathfrak{G}}$ versus G on logarithmic paper and the exponential values of the power law fluids are tabulated in Table (6.7). The difference between the two values may come from many sources. The molten polymers do not follow the power law exactly, hence n^(*) is obtained with uncertainty. Secondly, because of the crudeness of the experimental determination of B, the recoverable shear strain obtained from die swell of extruded polymers is also an approximated value.

		Tab	le 6.7	land a state of the state of th	
	M W		M _w /M _n	n ^(*)	n ^(**)
LDPE	53,500		3.0	0.44	0.37
HDPE	69,500		4.17	0.56	0.20
POLYPRO.	287,000	×.		0.50	0.31
POLYSTYRENE	320,000		3.1	0.27	0.32

(*) Exponent of power law fluid obtained from the plot of T_w versus G on logarithmic paper.

(**) Slope of the plot $\overline{\mathbf{0}}$ versus G on logarithmic paper for long capillary L/D= 25.

The plots of $\overline{O_{1/p}}$ versus G for short capillaries have the tendency to shift upward (Fig 6.10 to 6.13). This phenomenon clearly indicates a change of recoverable shear strain along the capillary.

To elucidate the phenomenon, the relationship between recoverable shear strains for short and long capillaries is obtained as following: Let $\bar{\sigma}_{\infty}$ and $\bar{\sigma}_{L/D}$ be the recoverable shear strains for infinitely long capillary and the one with dimensions ratio L/D respectively.

The plots of $Ln\left(\frac{\bar{\sigma}_{L/D}}{\bar{\sigma}_{\infty}}\right)$ versus (L/D) are shown in Figures (6.14)

to (6.15). The following equation is proposed for the relationship between $\bar{\sigma}_{\rm L/D}$ and $\bar{\sigma}_{\infty}$

$$Ln\left(\frac{\bar{\sigma}_{L}/D}{\bar{\sigma}_{ee}}\right) = A\left(\frac{L}{D}\right)^{a}$$
(6.10)

The data are best fitted by Equation (6.10). The constant A's and a's are tabulated in Tables (6.8) to (6.11)

It is interesting to notice that "a" depends only on polymer characteristics and nearly independent of pseudo shear rate (G)

"A" depends on shear rate (G) and equals to $Ln\left(\frac{\overline{\sigma}_{L/D}}{\overline{\sigma}_{\infty}}\right)_{L/D=1}$.

Equation (6.10) could be written as:

Ln	٥°	=	Ln(σ _{L/D})-	$A(\frac{L}{D})^{a}$
----	----	---	-----	---------------------	----------------------

(6.11)

TABLE 6.8

LDPE	$\bar{M}_{w} = 53,500$	M _w ∕M _n	= 3.00	T = 150°C
G(Sec ⁻¹)	3.8	12.8	38.0	128.0
А	1.35	1.59	1.8	2.05
a	976	970	925	- .954





HDPE:	₩ = 69,590	$\bar{M}_{w}/\bar{M}_{n} = 4.17$	T = 15	0°C
G(Sec ⁻¹)	12.8	38.0	128.0	386.0
А	.64	.78	1.02	1.32
a	790	805	795	814
	-		a an ann an Anna an Anna an Anna an Anna	an an tha an

TABLE 6.9

TABLE 6.10

 $\bar{M}_{W} = 287,000$ $T^{\circ} = 180^{\circ}C$ POLYPROPYLENE:

		A REAL PROPERTY OF A REAT		STATISTICS IN CONTRACTOR OF STATISTICS
G(Sec ⁻¹)	12.8	38.8	128.0	
А	1.35	2.2	2.8	
a	-1.46	-1.39	-1.37 °	

T A	DT	T	C	1	1
IA	DT	1 L	D	• 1	1

PO	LYSTYRENE (HF-	55)	₩ ₩ =	320,000 ^M _w / ^M n	= 3.1	$T = 170^{\circ}C$
	G(Sec ⁻¹)	5.8		19.3	58.0	
	А	1.4		1.4	1.6	
	a	-1.7		-1.36	-1.22	

The relationship between $\overline{\mathcal{G}}_{L/D}$ and $\overline{\mathcal{G}}_{c}$ could be used to estimate the die swell from short capillaries once ,"A" and "a" are obtained for a particular polymer. However, the relationships between A and a to polymer characteristics are still needed to be understood.

VII CONCLUSIONS

21

An INSTRON Rheometer has been used to study the polymer die swell. Based on the result of the experiment, the following conclusions could be made:

- 1) Die swell increases with shear rate
- 2) Die swell increases with shear stress
- Die swell of low density polyethylene is not affected by temperature
- 4) Die swell strongly depends on the distribution of molecular weights; the broader the distribution, the larger the swelling ratio.
- 5) Swelling ratio decays exponentially with the ratio length to the diameter of the capillary for all polymers studied
- 6) The importance of Deborah number in polymer processing is still unknown, however, die swell is not solely dependent on this number.
- 7) Recoverable shear strain for short capillaries could be estimated from the knowledge of its value at equilibrium and polymer characteristic, thus die swell for short capillaries could be calculated backward through the model, $\overline{O}_{-p} = f(d/D)$, for die swell

VIII SUGGESTIONS

7 .

* 7

.

2

.

-

- 1-

 It is observed that frozen effect of extrudate has made the exact value of swell diameter impossible to obtain. To overcome this difficulty, the extrudate polymer should be annealed in an inert oil.

- 2) Further work could be devoted to investigate the effect of molecular weight and molecular weight distribution on the exponential decay curve of die swell versus L/D. Standard polystyrene could be used to carry out this work. The mechanism of swelling process could be complicated, however, clear understanding the effect of molecular weight and molecular weight distribution on the decay of swelling could somehow elucidate the answer for the problem.
- 3) As a good try, we could follow the line suggested by Kawasaki (20) by using a better model to explain the die swell phenomenon.
 4) It is worthwhile to use standard polystyrene to investigate the effect of Deborah number on "die swell".

IX NOMENCLATURE

.

a	Constant defined by Equation (6.10)
A	Constant defined by Equation (6.10)
В	Die swell index (d/D)
В	Die swell index of zero length capillary
B _∞	Die swell index of infinite long capillary
c ·	Decay constant defined by Equation (6.5)
С	Polymer concentration
Cl	Constant in Mooney Equation (Eq. 3.7)
d	Extrudate diameter at extrusion temperature (inch)
d o	Diameter of extrudate polymer at room temperature (inch)
D	Capillary diameter (inch)
Eo	Entanglement density at zero shear
fb	Magnitude of force per unit cross-sectional area defined by Equation (3.12) (dynes/cm ²)
G	Pseudo shear rate (Sec ⁻¹)
Go	Elastic shear modulus (dynes/cm ²)
I ₁ , I ₂ , I ₃	Strain invariants defined by Equations (3.8) - (3.10)
Jo	Shear compliance (cm ² /dynes)
J _R	Rouse shear compliance defined by Equation (5.3)
к	Constant for power law fluid
k	Boltzmann's constant (erg molecule ⁻¹⁰ K ⁻¹)
L	Capillary length (inch)
Le	Entrance length (inch)
Ls	Length of steady state region in capillary (inch)
м	Molecular weight
M _n	Number average molecular weight
^M w	Weight average molecular weight
Mz	z average molecular weight
M 2+1	(z+1) average molecular weight

Ν	End correction in capillary flow
Na	Concentration in molecules per unit volume (cm^{-3})
n	Exponent of power law fluid
Р	Pressure (dynes/cm ²)
Q	Volume flow rate (inch ³ /sec)
R	Capillary radius (inch)
Rg	Ideal gas constant $(gm.cm^2 sec^{-2} g. mole^{-1}K^{-1})$
ta	Average residence time (sec.)
t _{xx}	Tensional stress defined by equation (3.16)
Т	Temperature (o _C or o _K)
Ϋ́	Velocity vector
v _r ,v ₀ ,v _z	Vector components of velocity (unit/sec)
Wi	Weight fraction of i - th component of polymer
Ŵ	Stored energy function

GREEK LETTERS

Ŷw	True shear rate at the wall (sec ⁻¹)
Γ	Pseudo shear rate
μ	Non-Newtonian viscosity (gm/cm.sec)
μ'	Dynamic viscosity
Θ	Time constant, general
θμ	Viscosity curve time constant, see Figure 6.5
Θμ	Dynamic viscosity.time constant, see Figure 6.5
θ	Time constant, Rouse theory
θ	Tobolsky time constant
θ	Time constant, William's theory
Θ	Time constant, Graessley's theory
θ _t	Average residence time (sec.)
λ	Extension ratio
¹ ¹ , ¹ ² , ¹ ³	Principal extension ratios
ρ	Density (gm/cc)
р _о	Density of frozen polymer (gm/cc)
σ	Recoverable shear
σ	Recoverable shear averaged over cross sectional area
σ _{L/D}	Average recoverable shear strain of capillary having L/D dimensions
ō 💩	Average recoverable shear strain of infinite long capillary
τ12	Shear stress (dynes/cm ²)
^τ 11 ^{, τ} 12	Normal stress (dynes/cm ²)
τ _t	Tensile stress (dynes/cm ²)
τ	True shear stress at the wall (dynes/cm ²)

X	REFER	RENC	CES
	1)	Ara	i, T. and H. Aoyama Trans. Soc. of Rheology., <u>7</u> , 333 (1965)
	2)	Bag	ley, E. B., J. Appl. Phys., <u>28</u> , 624 (1957).
	3)	Bag	ley, E. B. and H. J. Duffey, Trans. Soc. of Rheology, <u>14</u> (4), 545 (1970).
	4)	Bag	ley, E. B., A. A. Mendelson and F. L. Finger, Paper presented at National ACS Meeting, L.A. March 29, April 2, 1971.
	5)	Bag	ley, E. B., S. H. Storey and D. C. West, J. Appl. Polymer Science, 7, 1661 (1963).
	6)	Ber	nstein, E. B., A. Kersley and L. J. Zapas, Trans. Soc. of Rheology, <u>7</u> , 391 (1963).
	7)	Bey	non, D. L. T. and B. S. Glyde, Brit. Plastics, <u>33</u> , 414 (1960).
	8)	Bra	dley, R. S. "The phenonmenon of fluid motion" Addition Wesley, Canada (1967).
	9)	Bry	dson, J. A., "Flow properties of polymer melts" Van Nostrand Reinhold Co., New York (1970).
	10)	Bur	gess, H. and H. I. Lewis. Brit. Plastics, <u>34</u> (3), 177 (1961).
	11)	Cle	gg, P. L., Brit. Plastics, <u>39</u> , 96 (1966).
	12)	Col	eman, B. D. and H. Markovitz, J. Appl. Physics, <u>35</u> , 1 (1964).
	13)	Dil	lon, J. H. and N. Johnston, Physics, <u>4</u> , 225 (1933).
	14)	Edw	ards, R, Tappi, J. of Polymer Science 49 (4), 55A (1966).
	15)	Gra	essley, W. W., J. Chem. Phys., <u>47</u> , 1942 (1967).
	16a)	Gor	en, S. L., S. Middleman and J. Gavis, J. Appl. Polymer Science, <u>3</u> (9), 367 (1960).
	16b)	Gra	essley, W. W. and L. Segal, Macromolecules, <u>2</u> , 49 (1969).

REFERENCES CONT'D

17)	Graessley, W. W., S. D. Glasscock, and R. L. Crawley, Trans. Society of Rheology, <u>14</u> (4), 519 (1970).
18)	Harris, E. K., Ph. D. Thesis, University of Wisconsin, (1970).
19)	Huseley, T. W. and C. G. Gogos, Polymer Eng. Sci., <u>5</u> (3), 130 (1965).
20)	Kawasaki, Tatsusaka and Ono, Kokunski Kagaku, Vol. 30, No. 338, pp. 326-331 (1973).
21)	Kruse, R. L., J. Polymer Science, <u>2</u> (9), 841 (1964).
22)	Horie, M. M. Eng. Thesis, McMaster University, Hamilton. (1972)
23)	Lidorikis, S., M. Eng. Thesis, McMaster University, Hamilton.(1970)
24)	McInstosh, "Elastic effects in the extrusion of polymer solutions". Doctoral Thesis, Washington University, St. Louis, 1960.
25)	Metzner, A. B., J. L. White and M. M. Denn, Chemical Engineering Progress, 81, December 1966.
26)	Mooney, M.,"Rheology (F.R.Eirich, Ed.), Vol. 11., Academic Press, New York (1958).
27)	Nakajima, M., and M. Shida, Trans. Soc. Rheol., <u>10</u> (1), 299 (1966).
28)	Rogers, M. G., J. of Appl. Polymer Science, Vol. 14, 1679 (1970).
29)	Seiglaff, C. K., Soc. Plastics Engrs. Transaction, <u>4</u> (2), 129 (1964).
30)	Smelkov, R. E. and N. A. Kozulin, 2h. Prikl. Khim 35 (12), 2698, (1962).
31)	Spencer, R. S., R. E. Dillon, J. Colloid Sci., <u>3</u> , 163 (1948).
32)	Tanner, R. I., J. Polymer Science (A2), 8, 2067 (1970).
33)	Treloar, L. R. G, "The physics of rubber elasticity", Oxford University Press, (1967).
34)	Tobolsky, A. V., H. Mark, "Physical chemistry of High polymeric system", 2nd ed., Inter- science, N. Y. (1950).

REFERENCES CONT'D

- 35) Vlachopoulos, J., M. Horie, S. Lidorikis, paper presented at the ⁷ Knoxville meeting of the Soc. Rheol., (1971), to appear in Tras. Soc. Rheol
- 36) Wechsler, R. L. and T. H. Baylis, Mod. Plastics, <u>36</u>, 107 (1959).
- 37) Wilson, W. R. K., International Congress Technol. Plastic Process, Proc. Discuss., Amsterdam (1960).

38) Williams, M. C., J. Chem. Phys., 42, 2988 (1965). (1972)

APPE	NDIX I		EXPERIM	IENTAL DATA	CUDEMENTO		
			RESULTS OF EXPERT	MENIAL MEAS	SUREMENIS		
		Lo	w Density Polyethylen	ie (0701)			
		м w	= 51,300				
		Μ _w	$/\bar{M}_{n} = 3.72$				
		Te	mperature = 150°C				
L/D	Px (Dyne	10 s/	-6 $40/\pi R^{3}$ cm ²) (Sec ⁻¹)	d/D	(d/D)*=B	$(B^4 + \frac{2}{B^2} - 3)$	1/2
	1.	90	3.866	1.645	1.696	2.44	
	з.	62	12.880	1.924	1.984	3.60	
1	7.	63	38.660	2.095	2.160	4.38	
	14.	75	128.000	2.362(MF)	2.435	5.67	
	26.	70	368.000	MF			
	2	86	3 866	1 543	1 591	2 04	
	2 ·	57	12.880	1.643	1.700	2.46	
2 99	9	53	38,660	1.857	1,915	3.31	
2.55	19.	83	128.000	1.988	2.050	3.89	
	31.	79	386.000	MF			
	2	01	2 066	1 500	1 571	1 97	
	3.	111	12 880	1.524	1 718	2.52	
5 01	13	35	38 660	1 828	1 885	3.19	
J. UI	27.	46	128.000	1.933(MF)	1,993	3.98	
	42.	59	386.000	MF			
	6.	35	3.866	1.438	1.483	1.65	
	13.	79	12.880	1.533	1.581	2.91	
9.9	23.	20	38.660	1.613	1.663	2.28	
	41.	45	128.000	1.699	1.752	2.69	
	53.	69	386.000	MF			
	lı.	115	3 966	1 405	1 1118	1 53	
	4. Q	71	10 000	1 545	1 503	2 05	
8	18	16	38 660	1.662	1.713	2.51	
5	32	55	128-000	1.766	1.820	2.91	
	52.	13	386.000	-MF			
				(B)((B)((B))			

2.13

L/D POLYETHYLENE CONTINUED (0701)

L/D	Px (dyr	10^{-6} mes/cm ²)	$4Q/\pi R_{1}^{3}$ (Sec ⁻¹)	d/D	(d/D)*=B	$(B^4 + \frac{2}{B^2} - 3)$
	0.	954	3.866	1.334	1.425	1.45
	1.	888	12.880	1.443	1.510	1.76
16	3.	179	38,660	1.542	1.589	2.04
	5.	862	128.000	1.632	1.682	2.39
	9.	219	386.000	MF		
×						
	. 10.	810	3.866	1.367	1.390	1.33
	22.	060	12.880	1.443	1.487	1.67
20	38.	140	38.660	1.520	1.567	1.96
	68.	790	128.000	1.600	1.649	2.26
	108.	720	386.000	MF		
		•	500 30 50 00 130 mm m			
	1.0	300	3 866	1 3 2 11	1 365	1 24
	20	700	12 880	1 100	1 1113	1 51
011 0	20.	0.50	20 660	1.400	1 520	1 78
24.8	43.	950	38.000	1.4/4	1.520	2 15
	107	160	128.000	1.571	1.676	2.15
	127.	100	388.000	1.025	1.070	2.50
	,	270	2 966	1 0 9 5	2 047	3 87
	1 ·	510	10 000	2.303	2.047	5.37
20	2.	350	12.000	2.299	2.571	5.57
100	11	600	128.000	2.525	2.000	7 70
	14.	020	386.000	2.735	2.820	7.70
		- 5	•			
	T X10		Υ _w			
	(dyn/c	cm ²)	(Sec^{-1})			
	1.	36	3.800			
	2	80	17.000			
	4	51	51.800			
	7	41	173.100			

(*) Corrected for temperature difference

894.600

11.31

	Low De	nsity Pa	olyethylene	(0118)		
	M _w = 5	3,500				
	™ _w /™ _n	= 3.00				
	Temper	ature =	150°C			
L/D	$P \times 10^{-6}$	$\frac{\tau}{W}$ - 5	$4Q/\pi R^{3}$	d/D	d∕D*	$(B^4 + \frac{2}{P^2} - 3)$
	(dynes/cm /	XIU	(360)			Б
1	1.80 4.50 9.50 5.00	1.60 3.30 5.10 6.25	3.866 12.880 38.660 128.000	1.533 1.815 2.019 2.190	1.619 1.917 2.133 2.813	2.15 3.31 4.26 5.09
	30.07	1.31	386.600	MF	MF	
2.99	2.6 6.5 12.0 25.5 40.2		3.866 12.880 38.660 128.000 386.600	1.436 1.606 1.748 1.861 MF	1.517 1.697 1.847 1.966	1.77 2.44 3.03 3.52
5.01	4.5 9.8 17.0 33.5 50.5		3.866 12.880 38.660 128.000 386.600	1.396 1.520 1.645 1.730 MF	1.475 1.605 1.738 1.827	1.62 2.10 2.60 2.94
8	7.1 13.0 23.1 43.0 63.5		3.866 12.880 38.660 128.000 386.600	1.350 1.459 1.550 1.640 MF	1.426 1.541 1.637 1.732	1.45 1.86 2.22 2.57
9.9	7.9 15.4 27.2 51.5 81.0	¢	3.866 12.880 38.660 128.000 386.600	1.332 1.422 1.505 1.590 MF	1.407 1.502 1.590 1.680	1.389 1.71 2.04 2.38
.6	13.5 26.0 89.5 68.0 108.0		3.866 12.880 38.660 128.000 386.600	1.300 1.310 1.447 1.524 MF	1.373 1.383 1.528 1.610	1.27 1.306 1.81 2.11

LOW DENSITY POLYETHYLENE (0118) CONTINUED

					3.40
L/D	Px10 ⁻⁶ (dynes/cm ²)	4Q/πR ³	d/D	d / D*=B	$(B^4 + \frac{2}{B^2} - 3)^{1/2}$
	15.4	3.866	1.285	1.357	1.215
	28.0	12.880	1.345	1.420	1.430
20	47.5	38.660	1.411	1.491	1.680
	81.5	128.000	1.489	1.573	1.980
	129.0	386.600	1.600	1.690	2.410
	18.5	3.860	1.282	1.354	1.20
	34.0	12.800	1.336	1.411	1.40
24.8	57.0	38.600	1.390	1.468	1.59
	103.0	128.000	1.461	1.543	1.87
	157.0	386.600	1.563	1.651	2.26
		*			
	.508	3.860	1.790	1.891	3.21
•	2.54	12.800	2.134	2.254	4.81
~0	5.53	38.600	2.410	2.546	6.27
	16.84	128.000	2.650	2.799	7.66
	26.16	386.600	2.708	2.860	8.07
	T ×10 ⁻⁵	:			
	WXIO	Yw_1			
	(Dvn/cm^2)	(Sec ¹)			

1.80	4.48
3.14	16.47
5.09	53.42
8.08	173.56
13.80	571.8

(*) Corrected for temperature difference

High Density Polyethylene (7930) $\bar{M}_{w} = 69,590$ $\bar{M}_{w}/\bar{M}_{n} = 4.17$

Temperature = 150°C

L/D	$P \times 10^{-6}$		$4Q/\pi R^3$	d/D	(d/D)*=B	$(B^4 + \frac{2}{3} - 3)^{1/2}$
	(byn/cm /					B ²
	. 0		3.866	1.804	1,906	2.65
	ц. Ц.7		12 880	1 986	2.098	4.09
0	2 73		38 660	2 325	5 2.050	5 80
0	2.70		128 000	2.020	3 010	8 90
	16 52		396 000	2.000	3 620	12 99
	10.52		300.000	5.450	5.020	12.55
	. 31		3.860	1.571	1,660	2.29
	1.71		12.880	1,777	7 1.870	3.12
1	4 45		38 600	2 055	7 2 170	д ц1
-	10 49		128 000	2.057	2 590	6 50
	20 98		386 000	2.450	3 050	9 1 5
	20.50		000.000	2.000	0.000	
	1.59		3.860	1.491	1.575	1.99
	3.49		12.800	1.650	1.740	2.61
2.99	8.45		38.600	1.830	1.930	3.36
	18.75		128.000	2.102	2 2.221	4.65
	33.69		386.000	2.54]	2.684	6.15
	3.05		3.860	1.448	1.529	1.82
	6.35		12.800	1.590	1.679	2.37
5.01	12.07		38.600	1.740	1.840	3.00
	24.79		128.000	1.970	2.080	4.02
	43.61		386.000	2.362	2.498	5.30
	4.45		3.860	1.410	1.560	1.93
	6.35		12.800	1.523	3 1.610	2.11
8	14.62		38.600	1.693	1.788	2.80
	29.88		128.000	1.899	2.006	3.68
	50.23		386.000	2.175	2.290	4.98
	4.45	,	3.860	1.390	1.468	1.60
	10.80		12.800	1.505	1.591	2.04
9.9	22.25		38.600	1.652	2 1.740	2.61
	43.23		128.000	1.850	1.950	3.46
	74.38		386.000			4.65.

HIGH DENSITY POLYETHYLENE (7930) CONTINUED

ť

L/D	Px10 ⁻⁶	$4Q/\pi R^3$	d/D	(d/D)*=B	$(B^4 + \frac{2}{2} - 3)^{1/2}$
	(Dyn/cm ²)				B
	6.99	3.860	1.385	1.463	1.58
	15.26	12.880	1.519	1.605	2.09
16	20.88	38.600	1.638	1.730	2.57
	58.49	128.000	1.805	1.900	3.25
	97.28	368.000	2.000	2.112	4.16
			·		
	12.71	3.860	1.375	1.450	1.54
	21.61	12.880	1.502	1.587	2.03
20	38.78	38.600	1.620	1.710	2.49
	71.84	128.000	1.774	1.874	3.14
	120.08	368.000	1.961	2.070	3.97
	.5.				
				•	
	12.71	3.860	1.375	1.468	1.60
	25.42	12.880	1.491	1.575	1.99
24.8	47.68	38.600	1.600	1.690	2.42
	95.45	128.000	1.740	1.840	3.01
	157.00	368.000	1.940	2.050	3.89
	- 5				
	τ.x10 σ	Y			
. ((Dyn/cm ²)	(Sec ⁻¹)			
((Dyn/cm ²)	(Sec ⁻)			

1.11	3.890
2.54	14.920
4.97	45.970
9.13	161.210
14.68	595.200

(*) Corrected for temperature difference

	Polypropyle	ene (PP-5820)			
	$\bar{M}_{w} = 287,00$	00			
	Temperature	e = 180°C			
· · · ·					
L/D	$Px10^{-6}$ (Dyn/cm ²)	40/mR ³ (Sec ⁻¹)		d / D = B	$(B^{4} + \frac{2}{B^{2}} - 3)^{1/2}$
	1.27	3.860		1.472	1.61
	2.48	12.800		1.703	2.47
0.99	4.45	38.600		2.082	4.02
	. 9.53	128.000		2.533	6.20
	17.80	386.000		3.133	9.67
•					
	2.09	3.860		1.350	1.16
	4.57	12.800		1.514	1.76
5.01	8.90	38.600		1.716	2.52
	16.63	128.000		2.036	3.83
	27.33	386.000		2.577	6.43
	3.49	3.860		1.330	1.12
	7.63	12.800		1.476	1.63
9.9	13.98	38.600		1.620	2.15
	25.43	128.000		1.880	3.17
		386.000			
-	13.35	3,860		1.300	1.07
	21.61	12.800		1,409	1.39
16	36.87	38,600		1.586	2.03
	58.48	128.000		1.807	2.87
	6.99	3.860		1.300	1.016
	14.62	12.800		1.448	1.53
20	25.43	38.600		1.565	1.95
κ.	44.50	128.000		1.794	2.82
	69.29	386.000	•		
	8.90	3.860		1.300	1.01
	18.43	12.800		1.452	1.53
24.8	31.78	38.600		1.575	1.99
	54.67	128.000		1.830	2.848
	83.91	386.000			
	$\tau_{1} \times 10^{-5}$	Y			
	w . 2.	w -1.			-xi
	(dynes/cm ⁻)	(Sec -) 4,58			
	1.57	16.50		*	
	2.60	48.60			
5	4.64	144.25			
	6.90	658.90			

	Polystyre	ne Commercial	HF-55		
	$\bar{M}_{w} = 320$,	000			
	$\bar{M}_w/\bar{M}_n = 3$.1			
	Temperatu	$re = 170^{\circ}C$			
L/D	Px10 ⁻⁶ (Dynes/cm ²)	$40/\pi R^{3}$ (Sec ⁻¹)		(d/D)*=B	$(B^4 + \frac{2}{B^2} - 3)^{1/2}$
0	.318 2.100 4.190 12.080	5.80 19.34 58.00 193.40		1.640 1.975 2.361 -MF	2.23 3.56 5.36
1	3.180 6.420 9.920 19.720	5.80 19.34 58.00 193.40		1.485 1.733 2.019 -MF	1.664 2.585 4.060
3	5.090 9.920 15.650 27.990 44.530	5.80 19.38 58.00 193.40 580.00		1.382 1.591 1.875	1.302 2.048 3.151
			5		
5	5.720 12.470 20.740 34.350 52.160	5.80 19.38 58.00 193.40 580.00		1.330 1.519 1.758	1.122 1.787 2.770
10	12.720 23.280 36.000 54.710 76.330	5.80 19.38 58.00 193.40 580.00	•	1.310 1.470 1.670	1.053 1.610 2.340
16.1	17.100 32.820 51.910 78.880 108.800	5.80 19.38 58.00 193.40 580.00		1.295 1.457 1.626	1.002 1.565 2.178
20	22.900 42.360 64.630 96.690 130.400	5.800 19.380 58.000 193.400 580.000		1.291 1.445 1.606	.990 1.520 2.100

POLYSTYRENE COMMERCIAL HF-55 CONTINUED

L/D	Px10 ⁻⁶	$40/\pi R_{1}^{3}$	(d/D)*=B	$(B^4 + \frac{2}{3} - 3)^{1}$	/2
	(Dyn/cm ²)	(Sec)		BZ	
	31.87	5.80	1.300	1.019	
	53.81	19.38	1.450	1.540	
24.8	79.90	58.00	1.597	2.070	
	117.68	193.40			
	159.03	580.00			
	τ×10 ^{- 5}	Ŷ.,			
	w	- N	*		
	(Dyn/cm^2)	(Sec ⁻¹)		÷	
	2.90(3.05)	5,80			
	4.98 (5.09)	28.35			ся.
	7.31	84.07		٥	
	10.22 (10.32)	341.58			
	12.83 (13.30)	681.60			

(*) Corrected for temperature difference.

Commercial Polystyrene (HT42-1) Temperature = 170°C

•

L/D	$Px10^{-6}$ (Dyn/cm ²)	$4Q/\pi R^3$	(d/D)*=B	$(B^4 + \frac{2}{B^2} - 3)^{1/2}$
	1 50	F 00	1 750	0.000
	1.39	5.80	1.753	2.000
0	5.72	19.38	2.076	4.004
	9.86	58.00	2.461	5.830
	.19.08	193.80		
		5.00		
	4.13	5.80	1.505	1.735
	9.54	19.38	1.762	2.770
1	17.17	58.00	2.088	4.050
	29.89	193.80		
	50.89	580.00		
				9
	7.31	5.80	1.379	1.291
2 99	13.99	19.38	1.599	2.080
2.55	22.26	58.00	1.850	3.050
	36.26	193.80		
	14.31	5.80	1.312	1.060
_	26.08	19.38	1.478	1.640
8	40.07	58.00	1.659	2.300
	61.07	193.80		
	92.24	580.00		
	20.67	5.80	1.320	1.088
0 0	34.98	19.38	1.472	1.620
5.5	50.25	58.00	1.643	2.242
	73.79	193.80		
				2
	28.30	5.80	1.312	1.060
16 1	48.98	19.38	1.441	1.508
TO'T	70.61	58.00	1.593	2.056
	102.40	193.40		
	34.66	5.80	1.310	1.053
20	58.52	19.38	1.429	1.470
	85.88	58.00	1.581	2.010

COMMERCIAL POLYSTYRENE (HT42.1)

L∕D	$Px10^{-6}$ (Dyn/cm ²)	4Q/πR ³	(d/D)*=B	$(B^4 + \frac{2}{B^2} - 3)^{1/2}$
24.8	42.30 71.88 106.87	5.80 19.38 58.00	1.310 1.430 1.593	1.053 1.470 2.056
	-5	193.80		
	τ _w xl0 (Dyn/cm ²)	(Sec ⁻¹)	the second	
	4.13	7.54		
	9.51 12.70 17.10	98.77 485.30 892.80		

(*) Corrected for temperature difference

DATA TO INVESTIGATE TEMPERATURE EFFECT ON DIE SWELL OF LOW DENSITY POLYETHYLENE

Low De	insity Polyethylene		
	3,500		
[™] w/ [™] n	=		· *
T = 15	o°c	Ŧ	
L/D =	40		
G (pseudo S	shear rate) ec ⁻¹	Force (1b)	Die Swell (d/D)*
		•	
T=150°C 3	. 86	57.3	1.223
12	.80	98.0	1.245
38	2.00	273 0	1.291
386	.00	428.0	1.378
T=170°C 3	.86	37.3	1.221
12	. 80	71.0	1.243
38	1.60	122.0	1.297
128	.00	212.0	1.327
386		345.0	1.384
m-100 ⁰ 0	0.0	0 11 2	1 017
1=190 C 3	80	24.3	1.217
38	- 60	72.0	1.255
128	3.00	165.0	1.291
386	.00	278.0	1.354
0			
T=210°C 3	.86	16.3	1.096
12	. 80	36.0	1.100
38		68.0	1.280
128	.00	218 0	1.313 1.374
560		210.0	1.0/7

(*) Corrected for temperature difference